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Congo red removal by PANi/Bi_2WO_6 nanocomposites: Kinetic, equilibrium and thermodynamic studies

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ABSTRACT

Polyaniline/Bismuth tungstate (PANi/Bi_2WO_6) nanocomposites were synthesized by a facile chemical method. The prepared samples were characterized using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), X-Ray Energy dispersive Spectroscopy (EDS) and Scanning electron microscopy (SEM). Bismuth tungstate co-modified by PANi was used as an eco-friedly adsorbent to remove anionic dye Congo red (CR) from aqueous solution. The obtained experimental results showed that the CR dye removal efficiency is significantly dependent on different physico-chemical conditions including initial pH, contact time, PANi weight content in PANi/Bi_2WO_6 nanocomposite, adsorbent dose, CR initial concentration and temperature. It was found that The CR adsorption efficiency increased from 13.74 to 92.03% for when the PANi content coated on Bi_2WO_6 nanoparticles was increased from 0 to 10 wt.%, respectively. This was explained by improvement in the amino groups of PANi, the creation of porous nanostructures and the increases in the specific surface area and decreases mean particle sizes. In addition, the experimental kinetic results were fitted by the pseudo-second-order model. Also, the equilibrium data were best represented by Redlich-Peterson and Langmuir isotherm models. The thermodynamic parameters indicate that the adsorption process was spontaneous and endothermic in nature. Furthermore, the adsorption capacity PANi/Bi_2WO_6 for CR dye was not significantly affected during four regeneration cycles.

1. Introduction

Water pollution has increased surprisingly these past decades and become one of the most serious environmental problems which constantly threatens the human health and sustainable development of society. The colored effluents are known as a major source of aquatic ecosystem pollution related to different dye manufacturing industries. It is well known that the many of the synthetic dyes are toxic and non-biodegradable [1]. So, to solve the questions related to water pollution, many researchers worldwide have developed low coast materials to prevent the increasing water pollution crisis, the adsorption procedure [2] is one of the effective ways to decompose pollutants with high toxicity from wastewater [3]. The advantages of this method comparing to other methods (i.e photocatalysis and electrochemical oxidation) is the simplicity of the process, flexible, economical technique and it is simple to implement and easy to operate.

Recently, the conducting polymers such as polyaniline (PANi), polypyrrole (PPy), polythiophene (PTh) and their composites have been considerable interest in multidisciplinary application fields including energy storage devices, photovoltaic cells, gas sensors, catalysts, protection against corrosion and wastewater treatment [4–8]. Among these conducting polymers, the PANi is a well-known polymer used because of its good redox reversibility, good conductivity, low cost, ease of preparation, non-toxicity, and better stability in the environment [9]. According to its oxidation state, the PANi exhibit three forms namely: leucoemeraldine base (completely reduced state, Y = 1), pernigraniline base (completely oxidized state, Y = 0) and emeraldine base (semi-oxidized state, Y = 1/2) [9]. The emeraldine base form may be transformed to emeraldine salt form by protonation/doping of amine groups in acidic medium. However, The PANi emeraldine salt based composites such as PANi/silica [10], PANi/Fe_3O_4 [11], PANi/montmorillonite [12], PANi/attapulgite [13] and PANi/$CoFe_2O_4$ [14] were successfully used as alternative adsorbents for wastewater treatment.

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Bismuth tungstate Bi_2WO_6 (BWO) is the simplest member of the Aurivilius family and it is a very promising material due its potential applications in different areas such as photocatalysis [15,16], luminescence, chemical inertness, photo-stability, and environmentally friendly features [17–20]. The PANi with an extended π-conjugated electron, has recently showed great promises [21] as it is supporter for the large specific surface area and the excellent electronic conductivity due to its important intrinsically conducting polymers.

In this study, we report the synthesis of PANi/BWO nanocomposites and their characterization, the PANi was coated into the BWO nanosheets with a simple chemical method. Structural, morphological and the removal efficiency of Congo Red (CR) pollutant in aqueous medium of the as-prepared nanocomposites were discussed and investigated.

2. Experimental

2.1. Chemicals

Aniline monomer (Sigma-Aldrich) was freshly distilled prior to use. The sodium persulfate $Na_2S_2O_8{\cdot}6H_2O$, hydrochloric acid HCl, nitric acid HNO_3, sodium hydroxide NaHO, bismuth nitrate Bi $(NO_3)_3{,}5H_2O$ (Sigma aldrich 99%) and ammonium tungstate $(NH_4)_{10}(W_{12}O_{41}){\cdot}6H_2O$ (Alfa Aesar 99.9%) were analytical grade and used without further purification.

2.2. Synthesis of the materials

2.2.1. Synthesis of BWO

We used the same method proposed by Alfaro et al. [22]. A typical synthesis procedure to elaborate the lutetium-doped Bi_2WO_6 samples can be described briefly as follows: a mixture of required amount of bismuth nitrate $Bi(NO_3)_3{,}5H_2O$ was dissolved in 50 mL of nitric acid (1 M) under vigorous stirring. Then, 50 mL of $(NH_4)_{10}(W_{12}O_{41}){\cdot}6H_2O$ solution (Alfa Aesar 99.9%) was added drop by drop to the Bi solution, with stirring for 2 h. Ammonium hydroxide NH_4OH (13 mol L^{-1}) was added in order to adjust the pH to 5.5. The solution was heated in a bath water at 80 °C, filtered and washed several times by distilled water and ethanol, and dried in the oven for a night at 80 °C. Finally, the resulting white solid was heated at 500 °C during 3 h. This temperature was selected after a series of thermal treatments to limit the crystal growth of particles.

2.2.2. Synthesis of PANi

The pure PANi was prepared by chemical oxidative polymerization of aniline monomer using sodium persulfate as oxidizing agent in hydrochloric acid solution (1 M). The equimolar mixture of monomer and oxidant was magnetically stirred for 12 h at 25 °C. Then, the greenish-black solid material obtained (PANi) was filtered and washed with distilled water and ethanol until the filtrate solution was colorless. Finally, the PANi powder was dried at 70 °C [23].

2.2.3. Synthesis of the nanocomposite

The PANi/Bi_2WO_6 was synthesized by chemical oxidative polymerization of aniline monomer in presence of Bi_2WO_6 nanoparticles in acidic solution. In a typical procedure, a certain amount of Bi_2WO_6 nanoparticles (0.80, 0.90, 0.95 and 0.99 g) was dispersed in 100 mL of HCl (1 M) by ultrasonic vibration for 30 min. Then, the aniline monomer was (10, 50, 100 and 200 μL, respectively) was added into the above mixture and treated by ultrasonic vibration for 30 min. After that, 50 mL of sodium persulfate solution (molar ratio of aniline/oxidant = 1/1) was slowly added dropwise to the mixture. The polymerization reaction continues under magnetic stirring for 12 h at room temperature. Finally the PANi/Bi_2WO_6 composites with different contents of PANi (1, 5, 10 and 10 wt.%) were filtered and washed with distilled water and ethanol several times to remove the soluble impurities, and then dried at 70 °C for 12 h. The color of Bi_2WO_6 particles was changed after polymerization reaction from blank to greenish-black, which indicates that the PANi was successfully deposited on the Bi_2WO_6 surface.

2.3. Characterizations

2.3.1. XPS analysis

The specimen surface composition of the pure PANI was analyzed using X-ray photoelectron spectroscopy (XPS, Shimadzu Co: AXIS ULTRA). The X-ray source was Mg Kα operated at 15 kV, the anodic current was 10 mA, the operating pressure in the vacuum chamber was lower than 5×10^{-7} MPa and the analysis area was 2 mm × 1 mm.

2.3.2. X-ray diffraction

The X-ray diffraction (XRD) patterns were collected using an EMPYREAN PANALYTICAL diffractometer operating at 45 kV/35 mA, using CuKα radiation with Ni filter, and working in continuous mode with a step size of 0,013°. Data suitable for Rietveld refinement were collected over a range 10–70° in 2θ. The crystallite size was calculated using the classical Scherrer approach (Eq. (1)):

$$\boldsymbol{D} = \frac{\boldsymbol{k}.\boldsymbol{\lambda}}{\boldsymbol{\beta}.\mathbf{cos}(\boldsymbol{\theta})} \quad (1)$$

in this expression, **D** is the coherence length (or average crystallite size), **λ** is the wavelength of the radiations (1.54056 Å for CuKα radiation), k = 0.9 for gaussian profiles, β is the angular broadening of Bragg peak due to size effect, and **θ** is the Bragg angle in Radians. The β value was calculated in the case of gaussian approximation of peak profiles:

$$\beta^2 = (\mathrm{FWHM})^2 - \omega^2 \quad (2)$$

where FWHM is the full width at half maximum of Bragg peak, and **ω** is the corresponding FWHM of the standard sample Bi_2WO_6

2.3.3. Microstructural characterization

Scanning electron microscopy (SEM) analyses were used to observe the morphology and the local composition of the polycrystalline material. The determination of chemical compositions was performed using Energy Dispersive Spectroscopy (EDS). Preliminary images were obtained with a SUPRA 40 VP COLONNE GEMINI ZEISS using a maximum voltage of 20 kV.

2.4. Adsorption experiments

The adsorption experiments of CR on the PANi/Bi_2WO_6 composite were carried out in a batch system. The adsorption tests were conducted in glass beakers (150 mL) containing 50 mL of CR solution at a constant agitation speed. The effects of experimental parameters such as pH, PANi/Bi_2WO_6 dosage, solid/liquid contact time, CR initial concentration and temperature on the adsorption process were investigated. The initial pH of the solution was adjusted by addition of HCl (1 M) or NaOH (1 M). The concentration of CR in the solution before and after adsorption tests was determined using a UV–vis spectrophotometer UV 2300 (Techcomp limited) at the wavelength of 497 nm. The adsorbed amount (Q_{ads}) and percentage removal (% Removal) were calculated using the following equations:

$$Q_{ads} = (C_i - C_e) \times V/m \ (\mathrm{mg/g}) \quad (3)$$